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(54) Improved invar alloy

(57) An alloy with a low thermal coefficient of expansion which comprises (by weight) 34.5–37.5% Ni, up to 0.1% C, up to 1.0% Si, up to 1.2% Mn, up to 0.025% P, up to 0.025% S, up to 0.05% Co, up to 0.5% Cr, up to 0.5% Mo, and up to 0.02% Al, the balance being Fe wherein the Mn content is 0.5–1.2% when either the S content or the Al content is more than 0.005%, is non-sensitive to stress corrosion cracking and high temperature cracking, is structurally very stable and maintains a low thermal expansion coefficient in the temperature range from room temperature to the temperature of liquefied natural gas i.e. − 162°C.

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Fig. 1

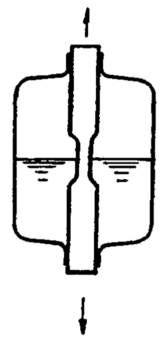


Fig. 2

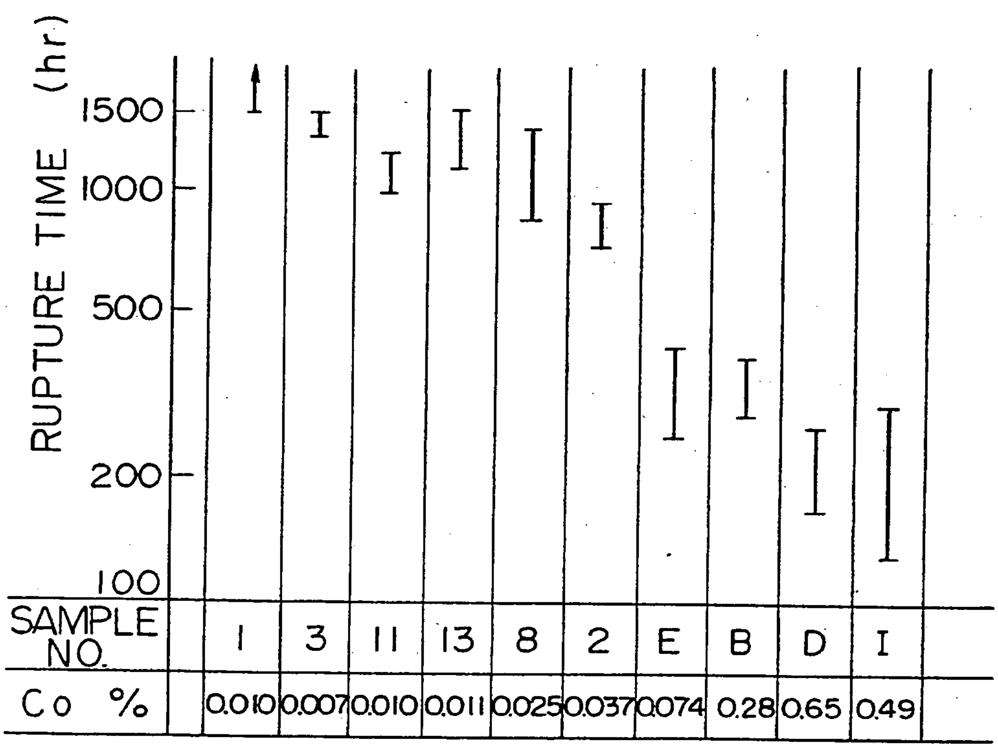
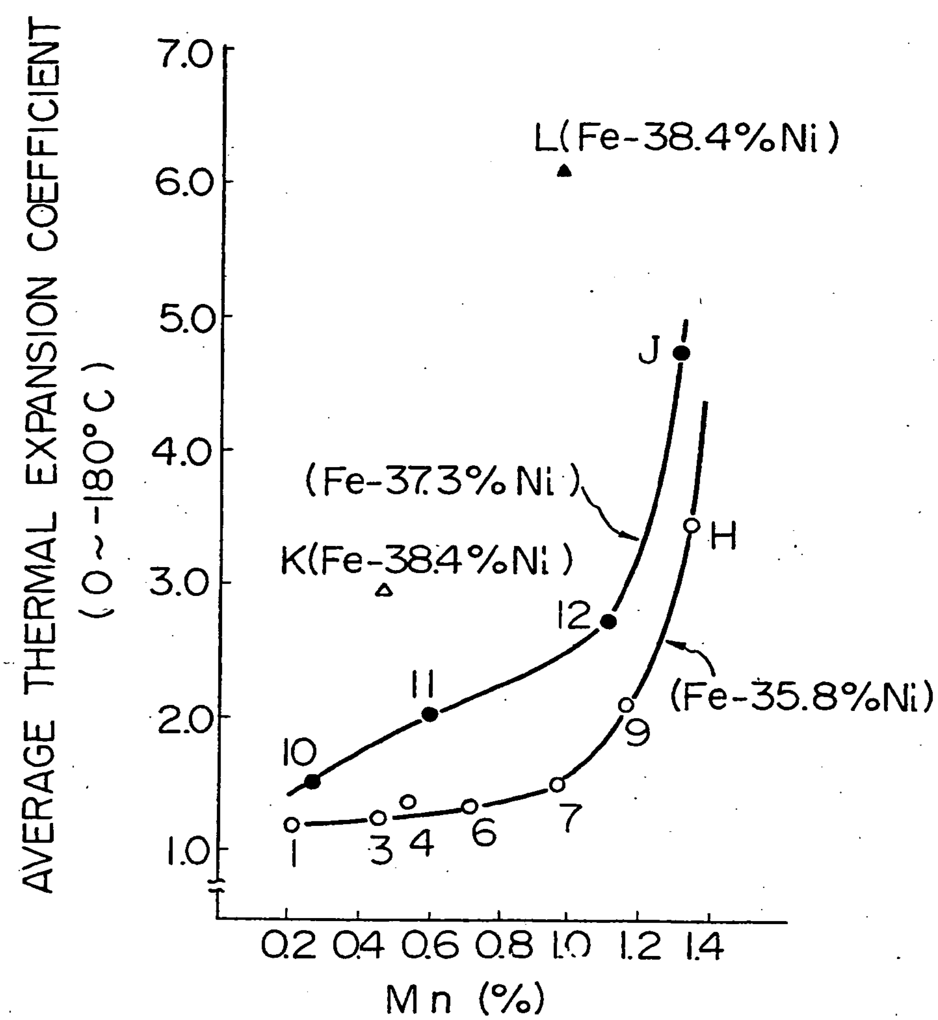

RUPTURE TIME (hr)
1500
1000
500
200
100
SAMPLE NO.
1 3 11 13 8 2 E B D I
Co %
0.010 0.007 0.010 0.011 0.025 0.037 0.074 0.28 0.65 0.49

Fig. 3



AVERAGE THERMAL EXPANSION COEFFICIENT
(0~-180°C)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
L(Fe-38.4%Ni)
J
(Fe-37.3%Ni)
H
K(Fe-38.4%Ni)
12
11
(Fe-35.8%Ni)
9
10
1
3
4
6
7
0.2
0.4
0.6
0.8
1.0
1.2
1.4
Mn (%)

SPECIFICATION

Improved invar alloy

Background of the Invention

This invention related to an improvement on the low termal expansion coefficient alloy commonly known as "Invar" (registered Trade Mark).

Invar, the typical low termal expansion coefficient alloy, according to the ASTM, comprises 35–37% Ni and the balance Fe, and may contain up to 0.5% of Mn, up to 0.5% of Co, up to 0.5% of Cr, up to 0.5% of Mo, up to 0.1% of C, up to 0.3% of Si, up to 0.025% of S and up to 0.025% of P as allowable additive elements and/or impurities. And a small amount of Al, which is used for deoxidation, may exist as the residue.

Generally speaking, in the high-Ni Fe–Ni alloys, activities of C, N and O are remarkably high because of the high Ni content, and in the course of solidification CO bubbles formed from C and O, and N_2 bubbles originated from dissolved N are generated, which result in formation of blisters in the formed ingots. These formed blisters make the hot working of the alloy impossible, and therefore, vacuum melting is usually employed in the production of Invar alloys.

As the high-Ni Fe–Ni alloys solidify in the form of the homogeneous austenite phase, impurities are liable to segregate. Such segregated impurities are not homogenized by heating in a soaking pit, and therefore they cause cracking in the course of slabbing (intergranular fracture), which constitutes another cause of difficulty in the hot working.

It was already reported that the intergranular fracture could be substantially prevented by limiting the S content to 0.05% or less, the Al content to 0.020% or less and the O content to 0.025% or less (Japanese Laying-Open Patent Publication No. 52922/76).

In the meanwhile, demand for the liquefied natural gas (hereinafter called LNG) has been remarkably expanded, and thus need for tankers, storage tanks, tank trailers, etc. and related large scale constructions for transportation and storage thereof as well as the equipments therefor (hereinafter referred to as "the containers and equipments") is increasing.

Characteristic properties required for the material for constructing these containers and equipments are: (a) That the metalographic structure of the material is stable over the temperature range down to −162°C, to which the material is exposed, and thus does not lose its toughness at this low temperature. (b) That dimensional change in the temperature range from room temperature of −162°C, to which the containers and equipments are exposed, is minimum, namely, the thermal expansion coefficient is sufficiently small in this temperature range. (c) That the welding work, which is indispensable for constructing the containers and equipments, can be easily carried out, and welding defect, that is, high temperature cracking, which will result in gas leak or breakdown of the containers and equipments, does not develop. (d) That the containers and equipments built of the material are not susceptible to delayed cracking such as stress corrosion cracking, etc.

There is no material that satisfactorily meets all these requirements. Among the materials which meet some of these requirements, there are 9%–Ni steel, aluminum alloys, austenite stainless steels, 36%–Ni Invar alloy, etc., which are now used as the materials for the containers and equipments for LNG.

The 36%–Ni Invar alloy satisfies (a) and (b) among the above-mentioned requirements. That is, this alloy maintains the metal structure of face-centered cubic lattice down to −196°C, which is the temperature of liquefied nitrogen and thus easily effected in a laboratory, and maintains its toughness without exhibiting the ductility-brittleness transition phenomenon, and thus retains sufficient toughness at this temperature. Also this alloy is characterized in that it retains low thermal expansion coefficient over a wide range from room temperature to −196°C.

In this alloy, if the vacuum melting is employed, the above-mentioned problem of residual bubbles can be solved, and hot work cracking caused by intergranular fracture can be prevented in accordance with the teaching of Japanese Laying-Open Patent Publication No. 52922/76. Although these difficulties are solved, the alloy has defects that it easily develop high temperature cracking when welded, and its corrosion resistance is rather poor and it cannot be used when stress corrosion cracking must be considered, because its nickel content is high and the nickel forms low melting compounds with sulfur, which is inevitably incidental to the raw materials. That is to say, the alloy does not satisfy the conditions (c) and (d).

We have for many years studied prevention of high temperature cracking in welding and stress corrosion cracking of the Fe–Ni alloys, and we have now invented a new Invar alloy which is provided with the above-mentioned characteristic properties (c) and (d) without sacrificing the properties (a) and (b).

That is to say, there is provided a new improved Invar alloy, of which the stress corrosion cracking sensitivity is remarkably reduced by restricting the Co content of 0.05% or less by means of careful selection of Ni source; the sensitivity to the high temperature cracking in welding is reduced by modifying the content of Mn and that controlling the Mn content

depending upon the content level of S and Al; and the low thermal expansion coefficient and stability in the structure are well maintained by defining the Ni content as 34.5–37.5% in relation with the amount of the Mn contained.

Summary of the Invention

According to this invention, in the Invar alloy which comprises 36% Ni and the balance Fe and may contain C up to 0.1%, Si up to 1%, Mn up to 0.5%, P up to 0.025%, S up to 0.025%, Co up to 0.5%, Cr up to 0.5%, Mo up to 0.5%, and Al up to 0.02% as allowable additives and/or impurities; an improved alloy, whereof the Ni content is 34.5–37.5%, the Co content is not more than 0.05%, and the Mn content is up to 1.2% when both the S content and the Al content are not more than 0.005%, and the Mn content is at least 0.5% and up to 1.2% when either of the S content or the Al content is more than 0.005%, is provided.

In the alloy of this invention, the Ni content range is a little more expanded than that specified in the ASTM. This is based on the finding that, in this alloy, in order to maintain the structural stability in the low temperature down to − 162°C, at least about 34.5% of Ni is required, and there is no increase in the thermal expansion coefficient in the aforementioned temperature range with the Ni content up to 37.5% in the relation with the amount of Mn which is added to the alloy in accordance with this invention.

Carbon may be contained in this alloy up to 0.1% as specified in the ASTM when the corrosion resistance of the alloy is not a critical problem. However, its content should preferably be as low as possible for the above-mentioned reason—generation of CO gas. The preferred content is less than 0.01%.

Silicon has undesirable effect in the high Ni Fe–Ni alloys leading to the high temperature cracking in welding. In this invention, however, the problem of the high temperature cracking has been solved by the increase in the Mn content within the Si content range according to the ASTM. The Si content is preferably less than 0.25%.

Manganese is added in the alloy of this invention in excess of the content specified in the ASTM in order to overcome the deleterious effect of S and Al. However, the upper limit of the Mn content is restricted to 1.2% because of the adverse effect of Mn on the low thermal expansion coefficient of the alloy.

Phosphorus has little influence upon the properties required in the alloy of this invention. Therefore, P is allowed to be contained up to 0.025% as specified in ASTM. The preferred P content is less than 0.01%.

Cobalt has been revealed to conduce to stress corrosion cracking. Therefore the content thereof is limited to not more than 0.05%. The preferable Co content is less than 0.03%.

Chromium is an impurity more or less coming from the raw materials. But this element has little influence upon the properties required in the alloy of this invention, and therefore, it is allowed to be contained up to 0.5%. However, the preferable alloy of this invention contains substantially no chromium.

In the alloy of this invention, little or no Mo will be contained, if it is not positively added. And it is not a necessary element and thus is not added. However, it has no deleterious effect if it is contained up to 0.5% as specified in the ASTM.

Aluminum has adverse effect on the low thermal expansion coefficient and the intergranular fracture. However, this element is effective for deoxidation and denitriding and a small amount of the Al used in the melting step remains. The prior art publication, e.g., the above-mentioned Japanese Laying-Open Patent Publication 52922/76, teaches that this element should be restricted to 0.02% or less. Al has also undesirable influence on the high temperature cracking in welding. However, in this invention, the deleterious effect thereof is overcome by addition of the specified amount of Mn.

A slight amount of O and N is inevitably involved. In consideration of the intergranular fracture, the O content should preferably be not more than 0.025%. Nitrogen is usually contained in the alloys of this kind to the extent of 0.04% or so. But the N content should be as low as possible, since it is a cause of blistering. The preferred N content is less than 0.01%.

The alloy of this invention is usually prepared by vacuum melting.

The correlation of the contents of S, Al and Mn will be made clear in the following description of specific embodiments of the invention.

Now the invention is illustrated by way of the working examples with reference to the attached drawings.

Brief Explanation of the Attached Drawings

Figure 1 is a schematic presentation of the apparatus used for the stress corrosion cracking text in this invention.

Figure 2 is a diagram showing the results of the stress corrosion cracking.

Figure 3 is a graph showing the relation between the Mn content and the average thermal expansion coefficient of the Invar alloys at lower temperatures.

Detailed Description of the Invention

The chemical analyses of the samples used in these examples are listed in Table 1. Samples 1–13 are of alloys of this invention, while samples A–N are comparative alloys.

Table 1
Chemical Analyses of Sample Alloys

	Sample No.	C	N	O	P	Si	Ni	Co	Mn	S	A1
Invention Alloys	1	<0.010	<0.010	<0.025	0.007	0.23	35.85	0.010	0.22	0.003	0.003
	2	<0.010	<0.010	<0.025	<0.005	0.17	35.96	0.037	0.29	0.004	0.004
	3	<0.010	<0.010	<0.025	0.006	0.21	35.79	0.007	0.47	0.003	0.004
	4	<0.010	<0.010	<0.025	<0.005	0.28	35.80	0.009	0.55	0.003	0.013
	5	<0.010	<0.010	<0.026	<0.005	0.16	36.01	0.010	0.65	0.011	0.003
	6	<0.010	<0.010	<0.025	<0.005	0.14	35.82	0.011	0.72	0.013	0.004
	7	<0.010	<0.010	<0.025	0.006	0.20	35.90	0.011	0.98	0.004	0.002
	8	<0.010	<0.010	<0.025	<0.005	0.25	35.64	0.025	1.02	0.004	0.019
	9	<0.010	<0.010	<0.025	<0.005	0.17	35.71	0.010	1.17	0.014	0.004
	10	<0.010	<0.010	<0.025	<0.005	0.21	37.34	0.011	0.27	0.002	0.005
	11	<0.010	<0.010	<0.025	0.005	0.25	37.40	0.010	0.61	0.009	0.004
	12	<0.010	<0.010	<0.025	<0.005	0.19	37.21	0.012	1.10	0.011	0.004
	13	<0.010	<0.010	<0.025	<0.005	0.21	34.72	0.011	0.24	0.004	0.005
Comparative Alloys	A	<0.010	<0.010	<0.025	<0.005	0.15	36.02	0.010	0.24	0.004	0.009
	B	<0.010	<0.010	<0.025	<0.005	0.22	35.56	0.28	0.27	0.010	0.008
	C	<0.010	<0.010	<0.025	0.006	0.19	35.94	0.012	0.28	0.015	0.003
	D	<0.010	<0.010	<0.025	0.007	0.23	35.61	0.65	0.30	0.009	0.002
	E	<0.010	<0.010	<0.025	<0.005	0.18	36.02	0.074	0.32	0.012	0.032
	F	<0.010	<0.010	<0.025	<0.005	0.18	35.91	0.010	0.41	0.002	0.016
	G	<0.010	<0.010	<0.025	<0.005	0.21	35.68	0.009	0.47	0.005	0.010
	H	<0.010	<0.010	<0.025	<0.005	0.16	35.70	0.011	1.32	0.004	0.003
	I	<0.010	<0.010	<0.025	<0.005	0.20	36.94	0.49	0.84	0.004	0.003
	J	<0.010	<0.010	<0.025	<0.005	0.19	37.21	0.010	1.29	0.013	0.028
	K	<0.010	<0.010	<0.025	<0.005	0.27	38.46	0.009	0.47	0.012	0.004
	L	<0.010	<0.010	<0.025	<0.005	0.24	38.30	0.009	0.96	0.012	0.012
	M	<0.010	<0.010	<0.025	<0.005	0.18	34.36	0.009	0.20	0.012	0.034
	N	<0.010	<0.010	<0.025	<0.005	0.14	34.01	0.015	1.04	0.012	0.008

Each sample was melted in a vacuum high frequency electric furnace of 10kg capacity, and cast. The cast specimen was forged at about 1150°C, and by repetition of thermal treatment and cold working, it was formed into plates of predetermined thickness (2.0mm and 1.0mm). Thereafter the specimen was finally subjected to a thermal treatment at 800°C for 10 minutes.

The control of the Co content was effected by combined use of ferronickel and electrolytic nickel. Manganese was added in the form of metalic manganese. In order to prepare low S level specimens the desulfuration was carried out by using lime and fluorspar.

Using these specimens and the apparatus schematically shown in Fig. 1, a stress corrosion cracking test was carried out and the results are shown in Fig. 2. The test solution was a 20% aqueous solution of NaCl containing 0.46N Cr^{6+}. The temperature was 45°C and the applied stress was 30kg/mm^2.

The test results show that the stress corrosion cracking has nothihg to do with Ni and Mn but largely depends on the amount of Co contained. Therefore, the Co content should preferably be as low as possible. Although the Co content can be lowered by strict selection of the Ni source, there is a limit as a matter of course and the allowable upper limit is 0.05%.

Cobalt has the same effect as Ni for the structural stability and ferronickel is far more inexpensive than electrolytic nickel. Thus economically it is advantageous to set the allowable limit of the Co content high. But it is essential to restrict the Co content in order to control the stress corrosion cracking sensitivity of the alloy.

We studied the high temperature cracking in welding by way of the arc strike test, and the results are summarized in Table 2. The text conditions were as follows. Current: 110A, arc length: 2mm and arcking time: 4 seconds.

Table 2
Results of Arc Strike Test

Sample No.	1	3	7	4	8	H	A	F	G	6	9	12	5	K	C
S (%)	0.003	0.003	0.004	0.003	0.004	0.004	0.004	0.002	0.005	0.013	0.014	0.011	0.011	0.012	0.015
Mn (%)	0.22	0.47	0.98	0.55	1.02	1.32	0.24	0.41	0.47	0.72	1.17	1.10	0.65	0.47	0.28
Al (%)	0.003	0.004	0.002	0.013	0.021	0.003	0.009	0.016	0.010	0.004	0.004	0.004	0.003	0.004	0.003
Result *)	○	○	○	○	○	○	X	X	X	○	○	○	○	X	X

*) ○: No cracking X: Cracking

From this table, the following three facts are learned.

(1) When the S content is 0.005% or less and the content of the residual Al is also 0.005% or less, high temperature cracking does not occur regardless of the Mn content.

(2) When the S content is 0.005% or less and the Mn content is not less than 0.5%, high temperature cracking does not occur even if the amount of the residual Al is large.

(3) When the S content is more than 0.005% but the residual Al content is not more than 0.005%, high temperature cracking is prevented, if the Mn content is not less than 0.5%.

Therefore it is concluded that the high temperature cracking which frequently occur in the high-Ni Fe-Ni alloy can be controlled by regulating the Mn content depending on the S level and the content of the residual Al. From this viewpoint, the higher the Mn content, the better. But it is restricted from the aspect of thermal expansion coefficient as explained below.

Fig. 3 shows the change of the average thermal expansion coefficient over the temperature range 0°C– − 180°C of the Fe–Ni alloys respectively containing 35.8 (± 0.10)% and 37.3 (± 0.10)% Ni when Mn content is varied. Also average thermal expansion coefficient of 38.4% Ni level alloys is shown.

From Fig. 3, it is learned that average thermal expansion coefficient is largely influenced by the contents of Ni and Mn and it becomes remarkably large when Ni content exceeds 37.5% and Mn content exceeds 1.2%.

We also studied the structural stability of the alloy at low temperature (− 162°C). Specimens were kept at − 162°C for 10 hours and thereafter formation of martensite was checked. The results are shown in Table 3. The amout of martensite was measured by point counting under an optical microscope.

Table 3

Amount of martensite after kept at − 162°C for 10 hours

Sample No.	1	13	M	N
Amount of martensite	0	0	5.2%	4.9%

From Table 3, it is learned that both Mn and Ni have influence on the formation of martensite, and at least 34.5% Ni is required in consideration of the case where the Mn content is low, in order to obtain Fe–Ni alloy with good structural stability that does not form martensite at − 162°C.

As has been described in the above examples, the Fe–Ni alloy used for the containers and equipments for LNG is largely restricted in composition. That is, in order to maintain the structural stability at low temperature (− 162°C), it must contain at least 34.5% Ni. Cobalt which is incidental to Ni must be restricted to 0.05% or less for the prevention of stress corrosion cracking.

For the purpose of keeping the thermal expansion coefficient low, the Ni content cannot exceeds 37.5%. Manganese is effective for the prevention of high temperature cracking in welding. But the content thereof must be not more than 1.2%. The high temperature cracking in welding largely depends on the S level and the amount of the residual Al, but it is completely prevented by addition of Mn in an amount determined by the content of S and Al.

CLAIMS

1. An Invar alloy which comprises (by weight) 34.5–37.5% Ni, up to 0.1% C, up to 1.0% Si, up to 1.2% Mn, up to 0.025% P, up to 0.025% S, up to 0.05% Co, up to 0.5% Cr, up to 0.5% Mo, and up to 0.02% Al, the balance being Fe; the Mn content being 0.5–1.2% when either the S content or the Al content is more than 0.005%.

2. An alloy as claimed in claim 1 which contains not more than 0.005% S, not more than 0.005% Al and up to 1.2% Mn.

3. An alloy as claimed in claim 1 which contains not more than 0.005% S, more than 0.005% Al and 0.5–1.2% Mn.

4. An alloy as claimed in claim 1 which contains more than 0.005% S, not more than 0.005% Al and 0.5–1.2% Mn.

5. An alloy as claimed in any one of the preceding claims which contains up to 0.3% Si.

6. An alloy as claimed in any one of the preceding claims which contains less than 0.25% Si.

7. An alloy as claimed in any one of the preceding claims which contains up to 0.02% P.

8. An alloy as claimed in any one of the preceding claims which contains less than 0.01% P.

9. An alloy as claimed in any one of the preceding claims which contains less than 0.01% C.

10. An alloy as claimed in any one of the preceding claims which contains less than 0.03% Co.

11. An alloy as claimed in any one of the preceding claims which contains less than 0.01% N.

12. An alloy as claimed in any one of the preceding claims which contains less than 0.025% O.

13. An alloy as claimed in any one of the preceding claims which contains substantially no Cr.

14. An alloy as claimed in any one of the preceding claims which contains substantially no Mo.

15. An alloy having a composition substantially as given herein for any one of Samples 1–13.

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